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INTENSIFICATION OF SINTERING OF LOW-MELTING CLAYEY ROCKS BY CHANGING THE PARAMETERS OF THE CALCINATION MEDIUM

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It is shown that when low pressure is created in the calcination zone as a result of the released gases (H_2 and CO) the gas medium becomes reducing, which promotes earlier reduction of the active forms of iron oxides and the formation of a glass phase, which intensify the sintering of clayey rocks.

At the present time the sintering process in the technology for producing ceramic articles is intensified by introducing low-melting components (fluxes) into the batch and by creating a reducing gas medium.

In regions of the country where there are no natural and technogenic forms of fluxing agents, the use of imported additives increases the cost of the raw materials and the price of the finished product, which is economically undesirable. There are a number of technological difficulties in creating an artificial reducing gas medium by continually feeding reducing gases into the calcination zone. It is difficult to maintain a reducing gaseous medium because of the large volume of the calcination zone, various thermal processes in which gaseous products are released, and the form of the fuel.

In this connection, finding and developing new technological methods and techniques for intensifying the sintering of ceramic slips is an urgent problem, solving which requires turning attention to the technological parameters of the calcination medium.

Analysis of the existing technologies used in the production of ceramic articles shows that, essentially, a single parameter — the temperature — is used to activate the sintering process. In practice, important technological components, such as the pressure and character of the gaseous medium, do not participate in the intensification of thermal processes. Consequently, the deliberate use of different parameters of the calcination medium to accelerate the sintering of ceramic slips is of scientific and practical interest. Investigations in this direction make it possible to understand more deeply how various parameters (temperature, pressure, character) of the calcination medium affect the sintering of ceramic slips and to determine the optimal range of the parameters which can be used to regulate structure formation and the properties of the articles obtained as a function of the quality of the initial materials.

In the present work it is suggested that the pressure of the gaseous medium in the calcination zone be changed in order to intensify the sintering of ceramic slips. The creation of low pressure (13.3 – 133.0 Pa or 0.1 – 1.0 mm Hg) makes it possible to decrease the volume content of nitrogen and oxygen from 77 and 22%, respectively, to 1% and less. Then, the gaseous products released from heated clayey rocks will predominate in the gaseous medium in the calcination zone. It has been found [1] that the same gases are released when low-melting clayey rocks are sintered at normal and reduced pressure: H_2, CO, CO_2, O_2, N_2, and SO_3. They are the products of the decomposition of organic materials, carbonates, iron and sulfide compounds, feldspars, and clayey minerals and the pyrolysis of water molecules.

The sintering of low-melting clayey rocks was investigated in the present work by changing the parameters of the calcination medium for the example of Sukpak montmorillonite and Ulug-Khovun hydromicaceous clays (Republic of Tuva). The chemical composition of the raw materials, which is distinguished by a high content of iron compounds and alkaline-earth elements, is presented in Table 1.

In performing this work, 25 mm in diameter and 25 mm high cylindrical samples were formed by the plastic method from samples of pulverized, dried, clayey rocks. Dilatometric tests were performed on 5 mm in diameter and 50 mm high samples. Heat-treatment was performed in a laboratory electric furnace at temperatures ranging from 100 to 1000°C

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TABLE 1

Clay	Mass content, %									
	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	calcination loss
Sukpak	54.54	13.64	0.81	6.22	7.09	0.42	1.80	1.61	0.18	9.18
Ulug-Khovun	57.89	16.70	0.80	8.24	5.14	2.01	2.12	0.91	0.50	6.45

with isothermal holding at the final temperature for 1 h. The laboratory furnace was covered with a special hood, and air was pumped from the beneath the hood to reduce the pressure. As a result, the pressure in the medium was varied from 133×10^3 to 13.3 Pa.

Data from the dilatometric, differential-thermal, gas, and x-ray phase analyses and the results of physical-mechanical tests were used to assess the sintering of clayey slips during calcination in a medium with altered parameters.

The change in the parameters of the calcination medium (pressure decrease and temperature increase) with the start of heating of the clayey rocks strongly affects the course of the thermal reactions. As the pressure decreases to 65 – 133 Pa (0.5 – 1.0 mm Hg) the organic substances in the Sukpak clay start to decompose at 150°C; this is indicated by an increase of the contents hydrogen (from 0 to 2.37%) and carbon monoxide (from 0.03 to 24.73%) in the gaseous medium; this was established by a gas analysis performed with a MKh-1323 mass spectrometer. It is well known that at normal pressure the decomposition of organic material starts at temperatures above 220°C.

The results of a gas analysis of Sukpak clay calcined at reduced pressure (Table 2) show that the gas medium inside and outside the material is a reducing throughout the entire calcination period (the total content of the active gases H_2 and CO fluctuates from 26 to 57%). In this connection, reducing the pressure changes another parameter — the character of the gaseous medium — as a result of the gaseous products which are released when the clays are calcined.

Decreasing the pressure of the calcination medium gives rise to early dehydration of iron hydroxides starting at temperature 280°C with formation of α-Fe_2O_3 [2]. A high content of gases (H_2, CO) and the presence of a solid coke residue of organic materials (carbon) in the inner layers of the calcined material result in reduction of Fe_3O_4 and FeO, which play an active role in the sintering of ceramic slips.

Earlier dehydration of low-melting clayey rocks is observed as the parameters of the calcination medium change. The removal of chemically bound water in Sukpak montmorillonite clay at reduced pressure starts at 370°C, which is 80°C lower than at normal pressure (Fig. 1). Dehydration of Ulug-Khovun hydromicaceous clay starts at 400°C at low pressure and 500°C at normal pressure, and is completed at 700 and 800°C, respectively. In addition, as the pressure decreases, the mass losses of Sukpak and Ulug-Khovun clays at reduced pressure are 10 – 15% greater than at normal pressure. This shows that the reactions which are associated with the release of gaseous and vapor products and with the reduction of low-valence iron oxides are completed to a higher degree.

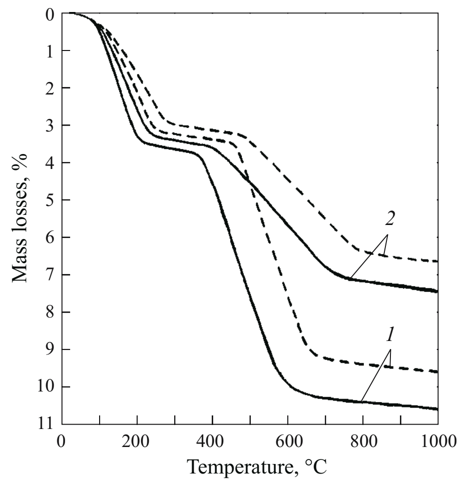

Fig. 1. Mass losses of Sukpak (*1*) and Ulug-Khovun (*2*) clays during calcination at reduced pressure (solid curves) and normal pressure (dashed curves).

The results of the dilatometric analysis performed with a change of the parameters of the calcination medium (Fig. 2) showed that as pressure decreases with a reducing gaseous medium, the formation of a glass phase and, correspondingly, the shrinkage of the Sukpak clay samples start at temperatures 70 – 80°C lower than at normal pressure. The same leading behavior of the shrinkage is also observed for Ulug-Khovun clay. A salient feature of the sintering of low-melt-

TABLE 2

Calcination temperature, °C	Gas content, vol.%					
	H_2	CO	CO_2	O_2	N_2	CH_2
150	2.37	24.73	17.35	15.47	39.26	0.72
250	3.84	57.13	19.32	4.08	15.70	0.61
350	5.14	52.14	24.58	3.17	14.01	0.54
550	5.84	49.14	39.94	2.14	9.13	0.30
750	8.14	30.14	56.59	0.89	3.04	0.17
950	22.37	19.32	55.53	0.63	1.17	0.15

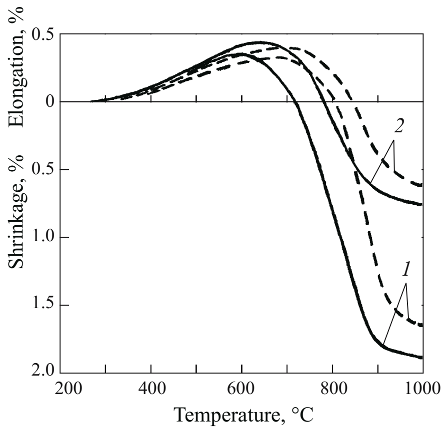

Fig. 2. Dilatometric curves for samples of Sukpak (*1*) and Ulug-Khovun (*2*) clays with calcination at reduced pressure (solid curves) and normal pressure (dashed curves).

ing clayey rocks with a change of the parameters of the calcination medium is that as the pressure decreases with a reducing gaseous medium, decomposition and amorphization of clayey materials proceed more intensively and are accompanied by the formation of an iron glass phase and new crystalline compounds.

Analysis of the dilatometric curves shows that as the parameters of the calcination medium change, the curves at the final stage gradually rectify and the shrinkage stops increasing. The increase of the length of this horizontal section shows that the interval of sintering of the slip increases as pressure decreases. The absolute magnitude of the shrinkage of the samples with a decrease of pressure is much greater than at normal pressure; this confirms the presence of intense shrinkage processes and densification of the ceramic material.

The intensification of the sintering of low-melting Sukpak and Ulug-Khovun clays at reduced pressure is due to the earlier and more intense formation of an iron glass phase, containing Fe^{2+}. It was determined that at reduced pressure with a reducing gaseous medium and the same calcination temperature the content of the glass phase is 30 – 50% higher than at normal pressure. The iron glass phase is more reactive and its dissolving power is elevated. Correspondingly, the increase of the fraction of the iron glass phase at reduced pressure is explained by the dissolution of free quartz and other refractory particles in it. As a result, the mechanical strength of articles calcined in a reducing medium at reduced pressure is much greater than for oxidative calcination at normal pressure.

As the data in Table 3 show, the Sukpak clay samples calcined at 900°C and reduced pressure in a reducing gaseous medium show volume shrinkage 7.0% and strength 53.7 MPa. The samples calcined at 1000°C and normal pressure show approximately the same shrinkage and strength. The results presented show earlier (by 80 – 100°C) onset of sintering of Sukpak clay in a reducing medium at reduced pressure. The high strength of the articles calcined in a reducing gaseous medium at reduced pressure is obtained not only as a result of a high content of the iron glass phase but also the formation of new, stable compounds which are not observed to crystallize at normal pressure.

Mössbauer spectroscopy and x-ray phase analysis showed the presence of wüstite FeO, iron spinels — fayalite, hercynite, iron metasilicate, and anorthite ($d/n = 0.320$, 0.252, 0.213 nm) in the phase composition of Ulug-Khovun clay samples calcined at 900°C and reduced pressure. These minerals increase the strength of the ceramic.

The strength of the articles calcined in a medium with altered parameters can be regulated by changing the residual pressure. It was determined that the strength of the calcined material gradually increases as the residual pressure decreases. The strength of Sukpak clay samples calcined at 900°C in a medium at various residual pressures is presented below.

Furnace pressure, Pa	Compression strength of the samples, MPa
1.33×10^5	42.4
1.33×10^4	44.7
1.33×10^3	47.1
133.0	53.7
65.0	62.5
13.3	73.8

In summary, the optimal pressure for calcination of articles made from low-melting clayey rocks should be in the range 65 – 133 Pa (0.5 – 1.0 mm Hg).

The results of the experimental investigations are confirmed by data from experimental tests performed at the en-

TABLE 3

Calcination temperature, °C	Reduced pressure			Normal pressure		
	volume shrinkage, %	water absorption, %	compression strength, MPa	volume shrinkage, %	water absorption, %	compression strength, MPa
800	4.1	17.7	41.3	3.2	21.2	35.6
900	7.0	12.5	53.7	5.6	16.4	42.4
1000	8.8	9.4	61.2	7.2	12.1	54.1
1100		Deformation		9.7	8.9	62.3

terprise "Tuvasuvenir," where the majolica articles from Sukpak clays, calcined in vacuum electric furnaces at 900°C had water absorption 14.8% with calcination at reduced pressure (133 Pa) and 17.1% with calcination at normal pressure. In addition, the articles calcined at low pressure were found to be impermeable to water and more heat-resistant (17 versus 10 cycles).

In closing, when heat-treating ceramic articles made from low-melting clayey rocks, to intensify sintering not only must the calcination temperature be increased but other technological parameters — the pressure and character of the gaseous medium — must be changed in a definite direction.

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